

Comparative study of the electron conduction in azulene and naphthalene

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Abstract. We have studied the feasibility of electron conduction in azulene molecule and compared with that in its isomer naphthalene. We have used non-equilibrium Green's function formalism to measure the current in our systems as a response of the external electric field. Parallely we have performed the Gaussian calculations with electric field in the same bias window to observe the impact of external bias on the wave functions of the systems. We have found that, the conduction of azulene is higher than that of naphthalene inspite of its intrinsic donor-acceptor property, which leads a system to more insulating state. Due to stabilization through charge transfer the azulene system can be fabricated as a very effective molecular wire. Our calculations shows the possibility of huge device application of azulene in nano-scale instruments.

Keywords. Azulene; Naphthalene; NEGF; Molecular Wire.

1. Introduction

Electron transport through a single molecule has generated a great deal of interest both theoretically and experimentally in recent times because of its wide variety of device applications(1; 2; 3; 4; 5; 6; 7). These types of molecules are believed to be the potential components of future nanoscale computational or electronic devices. Recent advances in experimental techniques have allowed fabrication and measurement of current through such nanoscale systems. Various molecules have already been demonstrated to behave as wires, switches, diodes, RAMs etc(8; 9; 10). In most of the experiments, the nanoscale material is an organic molecule or a π -conjugated polymer. Many theories too have been developed from empirical to semiempirical and *ab initio* level to describe the electrical response functions of the nanomaterials(11; 12; 13; 14; 15; 16; 17).

The ability of a molecule to switch between off and on states is one of the most important applications of these nanoscale materials. Experimentally, this has been observed in many organic molecules with various donor and acceptor substituents. Such unusual interesting behaviour of organic molecules with donor and acceptor moieties stimulates us to study the electronic conduction in azulene molecule and to compare that with its isomer, naphthalene. Although naphthalene and azulene are structurally similar with the same number of carbon and hydrogen atoms and the same number (*ten*) of π electrons, the properties of the azulene molecule differ from that of its isomer in many respects(18; 19; 20; 21). The geometry of the azulene molecule consists of fused five and seven membered rings which contributes to the intense blue color and the large dipole moment ($\mu = 0.8 - 1.08D$) for a hydrocarbon system(22; 23). It has interesting photophysical properties like $S_2 \rightarrow S_0$

fluorescence(24), large hyperpolarizability(25) etc. The observed dipole moment is due to the partial charge transfer from the seven membered ring to the five membered ring which gives the molecule aromatic stability obeying Huckel $4n + 2$ rule in both the rings with $n = 1$ and this gives the molecule intense blue color. Therefore, the ground state consists of a donor seven membered ring and an acceptor five membered ring fused together. On the contrary, naphthalene molecule consists of two fused six membered rings with six electrons in each ring. Here, there is no occurrence of charge transfer to gain aromatic stability which ensures the zero dipole moment and thus making it appear colorless.

Due to the interesting charge transfer properties of the two thiolated molecules, we have studied their I-V characteristics between two gold electrodes using the non-equilibrium Green's function methods, already widely reported in the literature. We apply the electric field along the principle C_2 axis in both the directions. Parallely, we use quantum chemical methods to study the effect of electric field on their molecular orbitals that are accessed during the transport.

In section II we have discussed about our computational details. Section III and IV contain the results with discussion and conclusion of our work respectively.

2. Computational Method

Firstly, to study the effect of electric field on the frontier molecular orbitals of both the molecules, we optimized the ground state structures of azulene and naphthalene with two thiol groups placed at the furthest positions as shown in fig.1 using the density functional methods with 6-31++G(d) basis set and density functional exchange correlation B3LYP. We then optimize the structures of both the molecules using the same basis set in

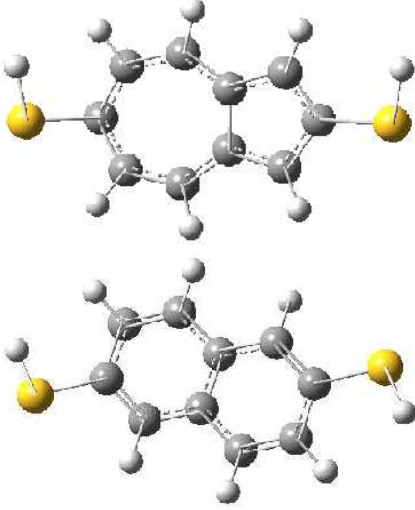


FIG. 1 Structure of azulene and naphthalene with two thiol groups linked at furthest positions

the presence of electric field, applied along the chain axis of the molecules. We vary the electric field in the interval of $0.001 a.u.$ and $1 a.u. = 5.142 \times 10^{11} \text{Volt/m}$. Vibrational analysis is then performed on each optimized structure to check whether, what we obtain are the stable minimum energy structures with all real frequencies. Then we calculate the Fock and overlap matrices for the ground state molecules which we use later for the calculation of current using non-equilibrium Green's function (NEGF) method(26). All calculations are performed with the standard Gaussian-03(27) package.

Parallely, we study the equilibrium properties of the molecules before connecting them with the electrodes. We first calculate the Green's function G in equilibrium situation using the formula,

$$G = \frac{1}{ES - H + i\eta} \quad (1)$$

where, E is the electron injection energy, S and H are the overlap and Fock matrices respectively. η is a small arbitrary broadening parameter arises mostly due to temperature. We get obtain S and H from the density functional calculations with Gaussian-03 package. The hydrogens attached to the thiol groups are removed by modifying the Hamiltonian and overlap matrices at those positions and these are then used for the calculation of the Green's function. From the eigen energies of the relaxed system, the Fermi energy, E_f of the electrodes is calculated assuming that it falls midway between the equilibrium highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energies of the molecule alone. The Fermi energy can be anywhere between the HOMO and LUMO and is generally considered to be a fitting parameter. Then we calculate the density of states and the transmission ($T(E)$) between the terminal sulfur atoms (S_1 and S_2).

$$T(E) \propto |G_{S_1 S_2}|^2 \eta^2 \quad (2)$$

The external electric field applied on the system has the form of a ramp potential, distributed over all the sites in such a way that the potential V_i at site i becomes $-\frac{V}{2} + V \frac{x(i) - x(S_1)}{x(S_2) - x(S_1)}$, where V is the applied voltage and $x(i)$, $x(S_1)$ and $x(S_2)$ are the x-coordinates of i -th atom, 1st and 2nd sulfur atoms respectively. This form of the potential ensures that the bias varies from $-V/2$ to $V/2$ across the molecule. The potential adds an extra diagonal term $\sum_i V_i a_i^\dagger a_i$ to the Fock matrix.

The effect of electrodes on the molecule has been incorporated through the well known self-energy term Σ for gold electrodes. With this imaginary self-energy terms the Hamiltonian gets modified as,

$$H = H_i + \Sigma_L + \Sigma_R \quad (3)$$

where H_i is the initial Hamiltonian for only the molecule. Σ_L and Σ_R are self-energies of left and right electrodes respectively. Having obtained the modified Hamiltonian, the current through the molecule is obtained using Landauer's formula(28),

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE [\text{Tr}(\Gamma_L G \Gamma_R G^\dagger)] \quad (4)$$

where Γ_L and Γ_R are the anti-Hermitian parts of the self-energy matrices, Σ_L and Σ_R respectively,

$$\Gamma_{L,R} = i(\Sigma_{L,R} - \Sigma_{L,R}^\dagger) \quad (5)$$

which describe the broadening of the energy levels due to the coupling of the molecule to the electrodes. The Green's function is obtained as the inverse of the modified Hamiltonian,

$$G = \frac{1}{ES - [H + i(\Sigma_L + \Sigma_R)]} \quad (6)$$

Using this Green's function we calculate the current. We calculate the transmission using the formula,

$$T(E) = \text{Tr}(\Gamma_L G \Gamma_R G^\dagger) \quad (7)$$

3. Results and Discussions

On application of electric field, the HOMO and LUMO of azulene changes from the ground state as can be seen from fig.2 and fig.3 respectively. These figures clearly

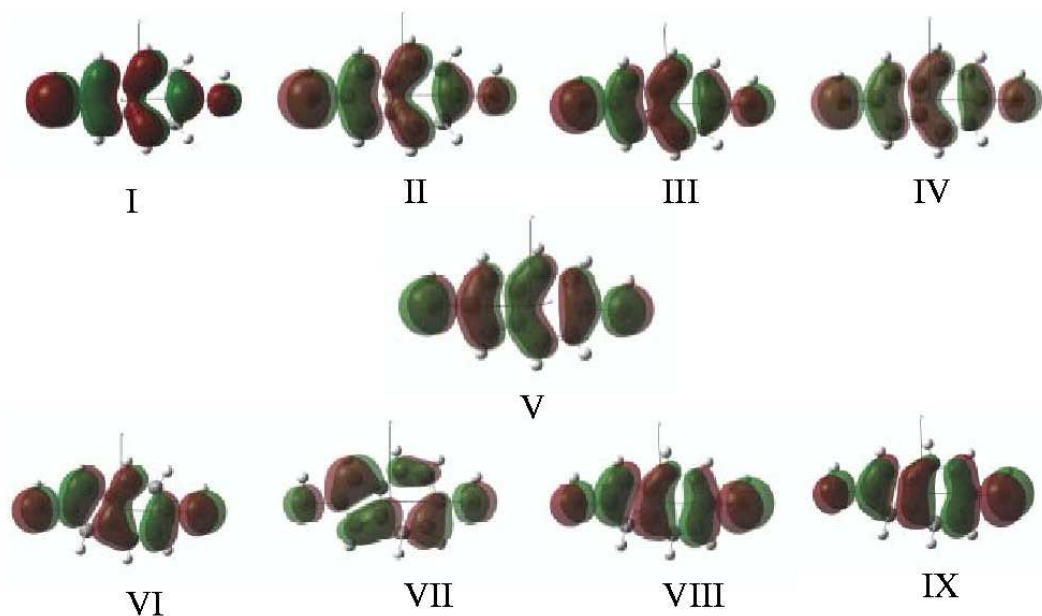


FIG. 2 HOMO plots for the electric fields 0.01 (I), 0.008 (II), 0.004 (III), 0.002 (IV), 0 (V), -0.002 (VI), -0.004 (VII), -0.008 (VIII), -0.01 (IX) for the azulene molecule with two terminal thiol groups (unit of electric field is a.u).

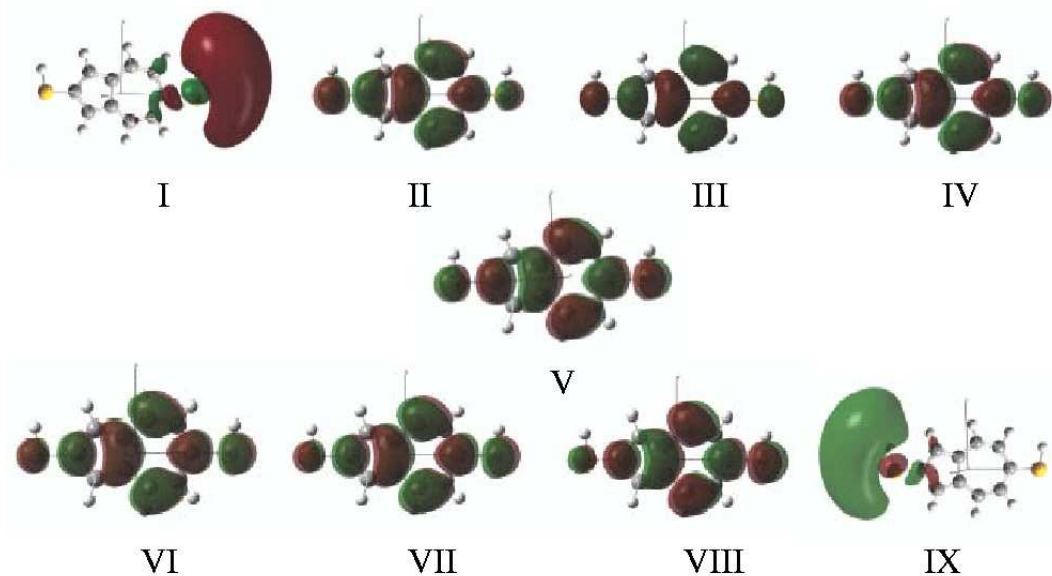


FIG. 3 LUMO plots for the electric fields 0.01 (I), 0.008 (II), 0.004 (III), 0.002 (IV), 0 (V), -0.002 (VI), -0.004 (VII), -0.008 (VIII), -0.01 (IX) for the azulene molecule with two terminal thiol groups (unit of electric field is a.u).

show that, the effect of electric field, applied along positive x-axis differs a lot from that along opposite direction. In case of HOMO, the electron density is delocalized over the whole molecule and it shows electron density shift along the bias direction. LUMO electron density is also delocalized but at higher bias value it shows complete localization of electron density at one end which depends on the bias direction. The ground state dipole moment also changes differently for the electric field in either directions. From the fig.4 it can be seen that, for both

the electric field directions, the dipole moment of azulene system increases. In absence of electric field the azulene molecule has some dipole moment which increases with increasing bias in positive x-axis direction. But the electric field along negative x-axis first reduces the dipole moment followed by a monotonic increase which can be seen clearly from the inset of fig.4. This observation is in agreement with the fact that the electron flows from the seven membered ring to the five membered ring. The electric field in the opposite direction forces the electrons

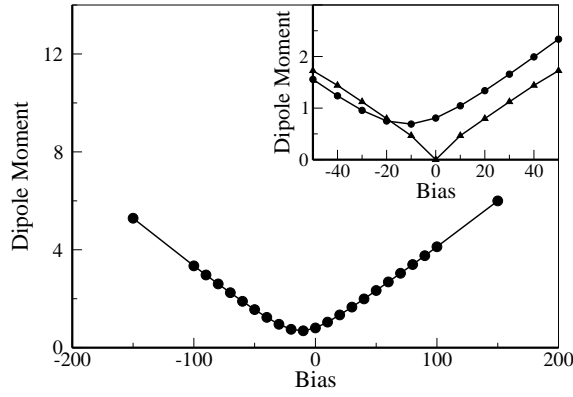


FIG. 4 Variation of dipole moment of the azulene system as a function of electric field. Inset shows the dipole moment for both azulene (*circle*) and naphthalene (*triangle*) in a smaller bias window.

to go from five membered ring to seven membered ring and thus the dipole moment reduces from the ground state dipole moment initially for lower bias. Further increase in bias in this direction accumulates the charge on the seven membered ring resulting in a dipole moment increase. But the dipole moment of naphthalene molecule increases with increasing bias in both the directions from the ground state zero dipole moment.

Fig.5 shows the variation of the energy of azulene system as a function of external electric field. The energy decreases with increasing electric field in $+ve$ x-axis, since the system gets stabilization for the charge transfer on application of electric field in this direction. But field along $-ve$ x-axis initially destabilizes the molecule at smaller bias values followed by a monotonic decrease in energy with increasing bias. The initial destabilization is attributed to the fact that, the small bias tries to force the electrons to flow in its direction in which the system loses its aromatic stability. But for larger bias values, the system again behaves like a charge transfer compound and starts getting stabilized. Inset of fig.5 shows the comparison of the energy variation of both azulene and naphthalene systems as a function of bias. The energy of naphthalene molecule decreases from the ground state energy on application of external bias, applied in both the directions.

So, it is clear from the above discussion that, the electron density rearranges differently for electric fields along $-ve$ and $+ve$ x-axis in case of azulene system, whereas in case of naphthalene system the effects of electric field along both the directions are same due to its symmetric structure. Now, we calculate the current as a response of applied electric field using the *NEGF* formalism for both azulene and naphthalene systems. First we plot the equilibrium, i.e., the zero bias density of states (*DOS*) in fig.6 and transmission in fig.7. From the *DOS* plot it can be clearly seen that the HOMO-LUMO gap in case of naphthalene ($\sim 4eV$) is higher than that of azulene ($\sim 3eV$) system. HOMO energy for naphthalene is lower

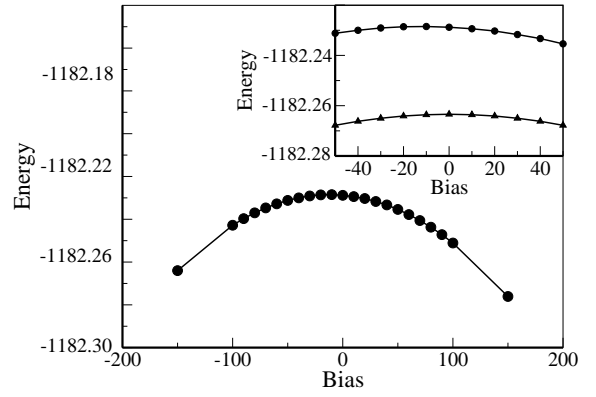


FIG. 5 Energy of the azulene system as a function of external electric field. Inset shows the energy for both azulene (*circle*) and naphthalene (*triangle*) in a smaller bias window.

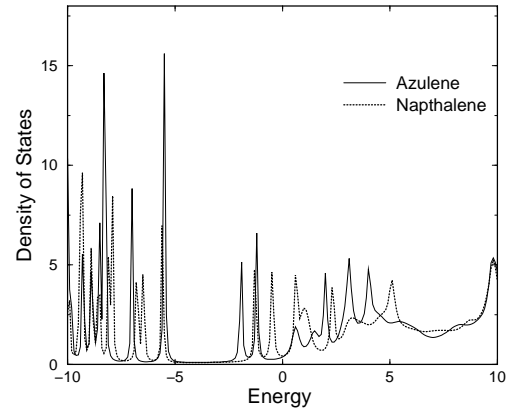


FIG. 6 Density of states as a function of energy for azulene and naphthalene molecules with two terminal thiol group.

than that of azulene and as a result, naphthalene is stabler than its isomer. From the plot of equilibrium transmission, it is very evident that, the HOMO of both azulene and naphthalene conduct well, whereas the LUMO of both show negligible transmission. Hence in our current calculations, we place the Fermi energy closer to the HOMO to probe conduction through the occupied levels.

To get proper molecular understanding, we keep the bias window more or less same for both types of calculations (*NEGF* and geometry optimization with electric field). In our calculations, the length scale of the molecules are $8 - 9 \text{ \AA}$, which ensures the bias window of Gaussian calculations similar to the *NEGF* calculations. Fig.8 shows the I-V characteristics with steps for both azulene and naphthalene systems. The I-V characteristics of naphthalene is completely symmetric in nature for both the bias directions, whereas for azulene it is not symmetric. It is very evident that, both the molecules show step-like behavior in I-V characteristics. These are the well known eigen-value staircases that appear whenever the electrochemical potential of the electrodes come in resonance with the molecular levels(1). We find that, in lower bias regime, both of them show nearly same cur-

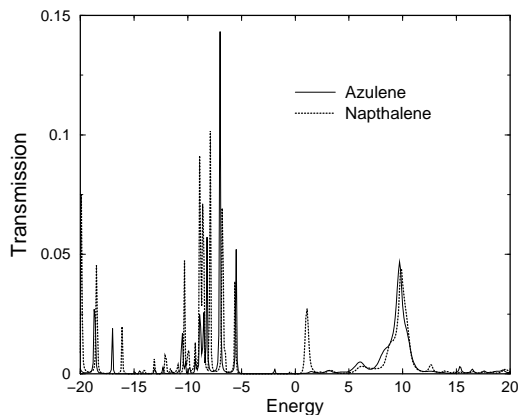


FIG. 7 Transmission as a function of energy for azulene and naphthalene molecules with two terminal thiol group.

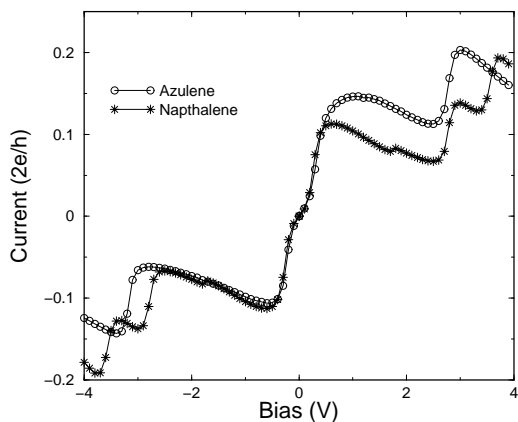


FIG. 8 Current as a function of bias for azulene and naphthalene molecules with two terminal thiol groups.

rent. Beyond a certain bias value along positive x-axis the azulene system shows more current than the naphthalene system. But for reverse bias the current of azulene system is lower than the naphthalene. It is due to the fact that, bias along +ve direction drives the electrons easily from seven membered ring to the five membered ring, whereas reverse bias drives the electrons opposite to the dipole moment direction. As a consequence, the current becomes lower than that of naphthalene which has symmetric electron cloud distribution over the two six-membered rings. At higher bias values the current shows a considerable decrease with increase in bias due to voltage induced localization. So, the interesting result, coming out of our calculations is that, the azulene molecule which has intrinsic donor-acceptor property, shows more current than naphthalene; though it is expected to show more insulating behavior.

4. Conclusion

We have performed both NEGF and Gaussian calculations for both azulene and naphthalene systems to measure the current passing through these systems on appli-

cation of external electric field. We have observed the electron density rearrangement in both the systems in presence of bias. In case of azulene, the electrons flow from seven membered ring to the five membered ring more easily resulting in more stabilization with increase in bias. But for reverse bias, initially the dipole moment decreases with destabilization of the system due to electron flow in opposite direction. Our NEGF calculations show higher conductivity in azulene than that of in naphthalene system. Our results reveal the possibility of potential device application of azulene as molecular wire in future nano-scale instruments.

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